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A QUANTITATIVE ASSESSMENT OF DIESEL GENERATED ACIDIC AEROSOLS IN UNDERGROUND MINES

FINAL REPORT

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INDEX

INTRODUCTION 1

RESEARCH PLAN 4

RESULTS AND DISCUSSION 7

Method Development 7

Selection of a filter 7

General Analytical Procedure 17

pH Analysis 17

Nitrate Ion Analysis 18

Sulfate Ion Analysis 21

Titrimetric Method 21

U.V. Method 26

Sulfate Ion, Nitrate Ion and pH Concentrations in Dieselized Underground Mines 35

Sulfate Ion 35

Nitrate Ion 47

pH Analysis 48

CONCLUSIONS AND RECOMMENDATIONS 57

EXPERIMENTAL 61

Sample Collection 61

Sample Preparation 63

pH Analysis 64

Analysis for Nitrate Ion 65

Analysis for Sulfate Ion 67

ACKNOWLEDGEMENTS 73

REFERENCES 74

INTRODUCTION

Catalytic converters have been installed on diesel engines used in underground mining in an effort to reduce the concentration of carbon monoxide and unburned hydrocarbons which are released as a result of the incomplete combustion of the fuel and to reduce the noise level in the mine environment. Although reducing the concentration of these substances in the exhaust is advantageous, the use of catalytic converters is of concern because several workers have shown that catalytic converters oxidize the sulfur dioxide produced in the burning of the fuel into sulfur trioxide (1,2) equation 1.

$$\text{Fuel S} \xrightarrow[O_2,\Delta]{} SO_2 \xrightarrow[\text{converter}]{\text{catalytic}} SO_3 \qquad [1]$$

Although the presence of sulfur trioxide (SO_3) would be of concern in the mine environment because of its very low TLV of 0.25 ppm (3), this substance is not a problem in underground mines because it reacts readily with the water vapour in the exhaust and/or in the mine air to produce sulfuric acid (1,2), equation 2.

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad [2]$$

This is of concern from a health point of view because the TLV for sulfuric acid is low, i.e., 1 mg/m^3 (3), and the sulfuric acid would be present as a fine mist or be absorbed

on the surface of the respirable sized soot particles emitted from the diesel engine (4). Obviously the sulfuric acid mist and/or the respirable sized particulate could be drawn into the lungs where the sulfuric acid would be deposited on the surface of the lungs. Since sulfuric acid would be destructive to the lung tissue, it is important to learn whether the sulfuric acid concentration is too high in the mine environment.

Two early studies by Kirk and Stefanich (5) and by Kirk and Seymour (6) attempted to assess the sulfuric acid concentration in underground uranium mines. Their work involved collecting both respirable and total dust samples which were analyzed for sulfate ion using a lead specific ion electrode. In addition, these workers determined the amounts of total resirable dust, TRD, respirable combustible dust (RCD), total dust (TD) and total combustible dust (TCD) in the mine environment where the sulfate samples were obtained. These workers assumed that the sulfate ion was directly related to the sulfuric acid concentration in the samples and thus to the sulfuric acid levels in the mine air, ie., it was assumed that all of the sulfate ion that was detected was present as sulfuric acid.

The studies by Kirk and co-workers showed that the sulfuric acid levels in the mine were finite and often exceeded the TLV concentration for sulfuric acid. For

example, the sulfuric acid on the respirable sized particulate ranged from almost zero to as high as 3 mg/m^3 or 3 times the TLV for sulfuric acid. In addition, the results from these studies indicated that approximately 80% of the sulfuric acid[1] was on the respirable dust samples. Since the sulfuric acid concentrations were above the TLV for sulfuric acid and since most of the sulfuric acid was associated with the respirable sized particulate, the sulfuric acid levels were of concern. The work in this contract was undertaken to learn whether the sulfuric acid levels were as high in another type of dieselized underground mine where catalytic converters are used and to try to determine how the sulfuric acid concentration varied with distance from the working face in a drift. This was important because the sulfur content of the diesel fuels and thus the sulfuric acid levels in underground mines is bound to increase as the amount of diesel fuel obtained from the high sulfur Alberta crude oils increases (7).

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[1] The ratio of H_2SO_4 respirable/H_2SO_4 total was 0.80 with a standard deviation of 0.26.

RESEARCH PLAN

The method developed by Kirk and co-workers (5,6) for determining the sulfuric acid levels in underground mines involved two basic steps (i) collection of the dust on a glass fiber filter and (ii) the analysis of the filter and dust for sulfate ion using a lead specific ion electrode.

The dust samples were collected on Whatman GF/A filters. Technical reports suggested that these filters are not suitable for determining the concentration of sulfuric acid because sulfur dioxide can be oxidized to sulfate ion on the glass fibers of the filters. As a result, a different type of filter was investigated to see whether a better filtering medium could be found. In addition, this study would provide some idea of the amount of oxidation of sulfur dioxide that occurred on the different filters.

The sulfuric acid analyses carried out by Kirk and co-workers were done by titrating the sulfate ion with a standard lead perchlorate ($Pb(ClO_4)_2$) solution using a lead specific ion electrode, equation 3.

$$Pb(ClO_4)_2 + SO_4^{=} \xrightarrow[H_2O]{CH_3OH} PbSO_4\downarrow + 2ClO_4^{=} \qquad [3]$$

This electrode only detected the free lead (Pb^{+2}) ion that was present in the sample. During the titration, ie., while there was sulfate ion in the solution, the Pb^{+2} ion from the lead perchlorate reacted with the sulfate ion to form

an insoluble precipitate of lead sulfate ($PbSO_4$) and thus the Pb^{+2} ion was removed from the solution. The precipitation of the lead sulfate was ensured by carrying out the titration in a 67% methanol (CH_3OH) water mixture where lead sulfate is less soluble. When all of the sulfate ion had been converted into lead sulfate, the concentration of the Pb^{+2} ion increased as more lead perchlorate was added to the solution. This excess Pb^{+2} ion caused a large change in the potential produced by the lead electrode. This jump in the potential indicated the end point for the titration.

Unfortunately, our initial investigations showed that there were several difficulties with this method. For example, the end point was often difficult to detect, particularly when low concentrations of sulfate ion were present. In addition, the end point for the titration was found to be pH dependent, eg., different results were obtained when one titrated standard samples of sulfuric acid and sodium sulfate containing the same amount of sulfate ion. Finally, this method of analysis was time consuming. As a result, a new spectrophotometric method was adapted and tested to see if a better analytical procedure for analyzing for the sulfate ion in dust samples collected underground could be found.

We also planned to increase the number of analyses that were carried out on the filters collected underground.

One other analysis we planned to perform on each filter was an analysis for nitrate ion. This was done to determine whether significant amounts of nitric acid were present in the mine environment. This was done because it seemed possible that nitric acid could have been formed from the nitrogen oxides and water in the catalytic converter. Finally, we planned to measure the pH of each filter in order to learn whether the total acidity was equal to that expected from the quantities of sulfuric and nitric acid found on the filters. The results of these investigations are discussed in the next section of the report. The detailed experimental methods used in all of these analyses are described in the experimental section of this report.

RESULTS AND DISCUSSION

Method Development

Selection of a filter:

One of the first problems that had to be addressed was the selection of a filter medium. Some recent technical reports suggested that SO_2 is oxidized to SO_3 which is then converted into H_2SO_4 on some filters, ie., that some of the SO_2 could be converted into sulfuric acid after it had been adsorbed on the fibers of the filter. In fact, one of the filters which was not recommended for collecting SO_2 for this reason was the Whatman GF/A filter used by Kirk and co-workers. As a result, we undertook an investigation of the Whatman GF/A filter and a Gelman spectrograde silica filter which was supposed to be able to collect SO_2 and retain it in an unaltered form. The actual control test involved pumping 38 liters of moist oxygen from one container and 38 liters of moist sulfur dioxide from a second container simultaneously through a filter at approximately two liters per minute with a personal sampler pump. Each filter and several blank (unused) filters were titrated using the lead specific ion electrode to determine whether any of the sulfur dioxide had been converted into sulfate ion (sulfuric acid) when the SO_2 was drawn through the filters. The results of these tests are shown in Table 1.

Table 1. Sulfate Analysis of Gelman Spectrograde and Whatman GF/A filters exposed and unexposed to 76 litres of a 50:50 mixture of sulfur dioxide and oxygen.

Filter	Unexposed ml of 2.5×10^{-3} M Pb^{+2} added at end point	Exposed to 76 l. of 50:50 $SO_2:O_2$ ml of 2.5×10^{-3} M Pb^{+2} added at the end point	ml of 2.50×10^{-3} M Pb^{+2} required to titrate the sulfate ion formed on the filter
Gelman	0.50		
Gelman	0.50		
Gelman	0.55		
Gelman	0.50		
Gelman	0.50		
	average 0.51 ml		
Gelman		0.85	0.34
Gelman		0.55	0.04
Gelman		0.75	0.24
Gelman		0.80	0.29
		average 0.74 ml	average 0.23 ml
Whatman	<0.05		
Whatman	<0.05		
Whatman	<0.05		
Whatman	<0.05		
	average <0.05 ml (1 drop)		
Whatman		0.175	<0.175
Whatman		0.180	<0.180
Whatman		0.170	<0.170
		average 0.175 ml	average <0.175 ml

The results in the second column of Table 1 show that the Gelman spectrograde filters give much higher blanks than the Whatman GF/A filters. In fact, the blank on the Gelman filter is approximately ten times (0.50 versus <0.05 ml of 2.50×10^{-3} M lead perchlorate solution) the blank observed for the Whatman filters. This means that the Whatman filters are superior from this point of view because the very low concentration or total absence of sulfate ion in the filters means that there can be little or no error arising from the presence of sulfate ions in the filters. This is an advantage because the filters are destroyed in the analysis and any sulfate on the filters would naturally be determined in the analysis.

The results in the last column of Table 1 also indicate that the Whatman filter should be used in this study. The amount of lead perchlorate solution that was required to titrate the sulfate ion on the filters exposed to the SO_2-oxygen mixture was at least 0.23/0.175 or 31 percent greater for the Gelman filter. This means that there was less oxidation of sulfur dioxide to sulfate ion on the Whatman filter and again one must conclude that the Whatman filter would give more reliable results in the sulfate analysis.

The Whatman filter was more attractive for other reasons as well. The Whatman filters were comprised of

individual glass fibers. These filters wet easily and moreover, the glass fibers readily separated from one another when they were stirred in water in the first step of the analysis. The Gelman filters on the other hand, were comprised of silica fibers that were coated with a plastic material. This made it impossible to wet the filters. This would make it difficult to expose all of the particulate to the solvent and thus to extract all of the sulfate ion (sulfuric acid) from the filter. In addition, the filters did not break up when they were stirred in water. This made it impossible to do control tests to determine whether the sulfate ion on the particulate could be removed from the filter. Thus experimentally, the Gelman filters were much harder to work with and might be difficult to extract ie., to remove all of the acid from the particulate because only a portion of the particulate would be exposed to the extracting solvent (water and/or the lead perchlorate solution).

Finally, blanks run on the two filters showed that the pH of the Gelman and Whatman filters were different. These experiments were carried out on the filters because one of the analyses that we required was a pH analysis that would indicate whether all of the sulfate and nitrate ions were present as sulfuric acid and nitric acid respectively. In these experiments, unused Whatman and

Gelman filters (blanks) were stirred for 10 minutes with 10 ml of deionized double distilled water. Although this was sufficient to break up the Whatman filter, the Gelman filter was still in tact at the end of this procedure (see above). Then, the pH of the resulting solution was measured.

An examination of the results in Table 2 shows that both of the filters are basic ie., have a pH of greater than 7.00. This conclusion was necessary because the solutions containing the filters had a higher pH (were more basic) than the deionized double distilled water that was mixed with the filter, ie., the water had a pH of 5.44±0.18 whereas the pH of the solutions containing the filters were 6.05 for the Gelman and 7.05 for Whatman filters respectively. In fact, the Whatman was considerably more basic than the Gelman filter because it consumed (titrated) more of the carbonic acid in the deionized double distilled water. In spite of the fact that the Whatman filter was more basic, the Whatman filter was the filter of choice because the filter and 10 ml of deionized double distilled water was neutral, ie., the average pH was 7.05. This meant that the acidity observed in a sample could be directly attributed to acid that had been collected on the filter. If the Gelman filter were used, one would have to correct for the acid present in the deionized

Table 2. The pH of Whatman GF/A and Gelman Spectrograde 25 mm filters.[a]

	pH Whatman GF/A	pH Gelman Spectrograde
Batch 1	6.90	6.05
	6.89	5.99
	7.19	6.20
		5.96
	average 6.99	average 6.05 ± 0.11[b]
Batch 2	7.13	
	7.00	
	7.16	
	average 7.10	

Total Average 7.05 ± 0.13[b]

a. The pH of the filter was determined by measuring the pH of the solution obtained after the filter had been stirred with 10 ml of deionized-double distilled water for 10 minutes. The deionized-double distilled water used in these analyses had a pH of 5.44 ± 0.18.

b. Standard deviation.

double distilled water-filter solution in determining the amount of acid in the sample collected on the filter.

Although the lower amount of oxidation of SO_2, the very small blank in the sulfate analysis, the ease of handling the filter experimentally and the pH of the filter all suggested that the Whatman GF/A filter was better for the series of analyses we wished to perform on the samples collected in dieselized underground mines, we decided to test the two filters on actual samples before the final choice of filter was made. As a result, a couple of respirable dust and total dust samples were collected on each filter in the dieselized 25 -29-30 stope at Falconbridge Nickel Company Limited's Strathcona Mine. During the 165 minutes of sampling an ST-2 Deutz diesel fitted with a PTX catalytic converter was mucking and dumping ore for 105 minutes. The duty cycle required approximately 1 minute. All the samples were collected in the same location, approximately half way (50 feet) from the mucking site and 50 feet from the dump site in the stope. The average results obtained for the Gelman and Whatman filters are presented in Table 3. The results from the individual filters are given in Table 4. An analysis of the data in Table 3 shows that the results are not very different on the two filters, ie., the average pHs are within 0.15 units, the average sulfate ion in the respirable filters

Table 3. A comparison of the pH, sulfate ion and nitrate ion concentrations found on the Gelman Spectrograde and Whatman GF/A filters collected in the 25-29-30 stope, Strathcona Mine, Feb. 17, 1982.

Filter	pH Respirable	pH Total Dust	mg/m^3 sulfate ion Respirable			mg/m^3 sulfate ion Total Dust			mg/m^3 Nitrate Ion	
			Titrimetric Method	U.V. method[a]	Average	Titrimetric method	U.V. method[a]	Average	Respirable	Total Dust
Gelman Spectrograde	6.74	6.66	Required less titrant than blank	0.38	0.38	0.16	0.69	0.43	0.003	0.44[d]
Whatman GF/A	6.80	6.81	0.25	0.35	0.30	0.48[b]	0.30[c]	0.39	0.004	0.66[e]

a. The analysis for sulfate ion using the U.V. method was done on the same sample after the titrimetric analysis was completed.

b. Only one value was used here. The other result of 2.25 mg/m^3 was found for the first filter we ever analyzed.

c. One of the three samples was analyzed in Inco Metal Company's laboratory at Copper Cliff, Ont.

d. Large errors were present in these analyses. The individual values were 0.88 and <0.001 mg/m^3.

e. Large errors were present in these analyses. The individual values were 1.88, 0.09 and <0.004 mg/m^3. The 0.09 mg/m^3 was found in a sample analyzed by another method in Inco Metal Companies Laboratory in Copper Cliff, Ont.

Table 4. The pH, sulfate ion and nitrate ion concentrations found on individual Whatman GF/A and Gelman Spectrograde filters collected in the 25-29-30 stope at Strathcona Mine, Feb. 17, 1982

Filter	pH	mg/m^3 Sulfate Ion		mg/m^3 Nitrate Ion
		Titrimetric method	U.V. method	
Whatman Respirable 1	6.81	0.19	0.27	<0.001
Whatman Respirable 2	6.79	0.30	0.43	0.007
Gelman Respirable 1	6.65	-	0.57	<0.002
Gelman Respirable 2	6.82	-	0.18	<0.004
Whatman Total Dust 1	7.23	2.25	0.28	1.88
Whatman Total Dust 2	6.38	0.48	0.43	<0.004
Whatman Total Dust 3	-	-	0.20[a]	0.094[a]
Gelman Total Dust	6.73	0.13	0.39	<0.001
Gelman Total Dust	6.66	0.19	0.99	0.88

a. Analysis done by Inco Metals Company, Process Technology Laboratory Copper Cliff, Ontario.

are within 27 percent, the average sulfate ion in the total dust samples are within ten percent, the average nitrate ion in the respirable dust are in complete agreement and the average nitrate ion in the total dust are within 33 percent even though the nitrate analyses are very inaccurate.

A closer examination of the results shows that the agreement between the results obtained in the two different sulfate analyses is much better for the samples collected on the Whatman filters. For example, the concentrations of the sulfate ion in the respirable dust samples and in the total dust samples were 0.25 and 0.35 (0.30 ± 0.05 mg/m^3) and 0.48 and 0.30 (0.39 ± 0.09 mg/m^3) respectively. Much larger discrepancies were observed for the Gelman samples, the sulfate ion concentrations were zero and 0.38 (0.19 ± 0.19 mg/m^3) for the respirable dust samples and 0.16 and 0.69 (0.43 ± 0.26 mg/m^3) in the total dust samples. It is interesting to note that in two of the three cases where a comparison can be made, the sulfate ion concentrations were lower on the Whatman filters than on the Gelman filters. This may have arisen because SO_2 is oxidized to sulfate ion more readily on the Gelman filter.

While the results are resonably similar for the two filters, it would appear that the results from the Whatman filters are more consistent. Although we cannot

explain why this is found, the greater consistency of the results, the smaller amount of oxidation of SO_2, the smaller sulfate blanks, the greater ease of handling and the more suitable pH of the Whatman filters, led the author to conlcude that the Whatman GF/A filters were superior for collecting particulate samples for pH, sulfate ion and nitrate ion analyses in dieselized underground mines.

General Analytical Procedure:

An initial investigation of the analytical methods available for determining the pH, sulfate ion and nitrate ion concentrations in aqueous solutions suggested that all these analyses could be done on the filters collected in dieselized underground mines if they were done in a particular order. The approach was to determine the pH with a pH meter, then to determine the nitrate ion using a nitrate specific ion electrode and finally to titrate the sulfate ion with lead perchlorate using a lead specific ion electrode to determine the endpoint. The development and testing of each of these methods is discussed in this section of the report.

pH Analysis:

The normal procedure for measuring the pH of a solution was used to determine the pH of the solution obtained when the filter was stirred (broken apart) in 10.00 ml of deionized-double distilled water. The two slight differences from the normal technique were i) that a small microprobe pH electrode

was used and ii) that a large number of blanks were measured. The small microprobe electrode was used so that the tip of the electrode could be immersed in the small volume of solution more easily and a large number of blanks were measured so that the pH of the solutions containing the filter could be related to the pH of the mine air. We believe that the pHs of the samples that we have analyzed are accurate to within the limits of the experimental error i.e., within 0.1 pH unit.

Nitrate Ion Analysis:

The nitrate analyses were carried out using a nitrate specific ion electrode in the normal manner (8); the concentration of the nitrate ion was determined from the electrode potential (MV reading observed) when the tip of the nitrate specific ion and reference electrodes were immersed in the sample. The concentration of the nitrate ion in the sample was obtained from a calibration curve relating the nitrate ion concentration to the electrode potential. Unfortunately, this analysis was not as accurate as one would like. The difficulty arose because the electrode response was quite different when the same standard solution was analyzed on different days, Table 5. This meant that we could not obtain a good stable calibration curve and thus we cannot guarantee that the nitrate ion concentrations are accurate. Although there were several changes in the method that could have been tried, we did not take the time to determine the source of the error and to

Table 5. The potential of the nitrate specific ion electrode in standard sodium nitrate solutions

Nitrate Ion Concentration in Moles/Liter	Nitrate Ion Electrode Potential in MV Feb. 17, 1982	Nitrate Ion Electrode Potential in MV Feb. 24, 1982	Nitrate ion Electrode Potential in MV March 29, 1982
1.0×10^{-6}	+120	+148	+101
1.0×10^{-5}	+111	+148	+82
1.0×10^{-4}	+107	+121	+104
1.0×10^{-3}	+86	+116	+96
1.0×10^{-2}	+37	+109	+53
1.0×10^{-1}	-7	-7	-4
1.0	-49	-50	-45

overcome the problem with the calibration curve or to develop a more reliable method for determining the amount of nitrate ion on the filters for several reasons:

First, the time was short and developing a new method or improving the specific ion electrode method would have meant that we would not be able to analyze as many samples from the mine.

Secondly, the nitrate ion analysis was not the most important analysis i.e., the work was initiated to determine the sulfate ion concentration and the pH of the samples collected underground. The concentration of the nitrate ion on the filter was additional information that was not essential.

Thirdly, even if a good calibration curve could have been obtained, it was realized that the MV readings obtained from the underground samples could still be incorrect because of differences resulting from interfering ions such as halide ions, cyanide ions, carbonate ions, sulfate ions, etc., and/or differences in the ionic strength of the mine samples and those used in preparing the calibration curve.

Fourthly, if other methods of analysis for nitrate ion were used, it would entail splitting the sample and/or adding several other reagents which would make it impossible to analyze the sulfate ion. Dividing the sample would make the analysis for sulfate ion more difficult because there would be even smaller amounts of sulfate in the samples. This would be a problem because the sulfate ion is already near the lower

limit of detection of the sulfate analysis.

Finally, the analysis of the filters collected underground indicated that the nitrate ion concentrations were very low in the underground mine environment. Thus an error of several hundred percent on a very low concentration does not change the concentration significantly, i.e., the nitrate ion concentrations are still very low even when a very large error is made in the analysis.

In the light of these difficulties, we decided not to spend the limited time developing a new method to analyze for nitrate ion. As a result, all of the nitrate ion concentrations have been obtained using the "average" calibration curve, Figure 1, and the concentrations of nitrate ion in this report are "approximate".

Sulfate Ion Analysis:

Titrimetric method:-Considerable time was spent learning the method for analyzing for sulfate ion. In fact, several different approaches were tried before we finally learned exactly how Kirk and co-workers (6) performed the analysis with the lead specific ion electrode and were able to determine the concentration of the sulfate ion in standard solutions. Once we had learned the basic technique, the next problem was to determine the best concentration for the lead perchlorate solution that was used to titrate the sulfate ions. This work involved preparing standard solutions containing different "known" amounts

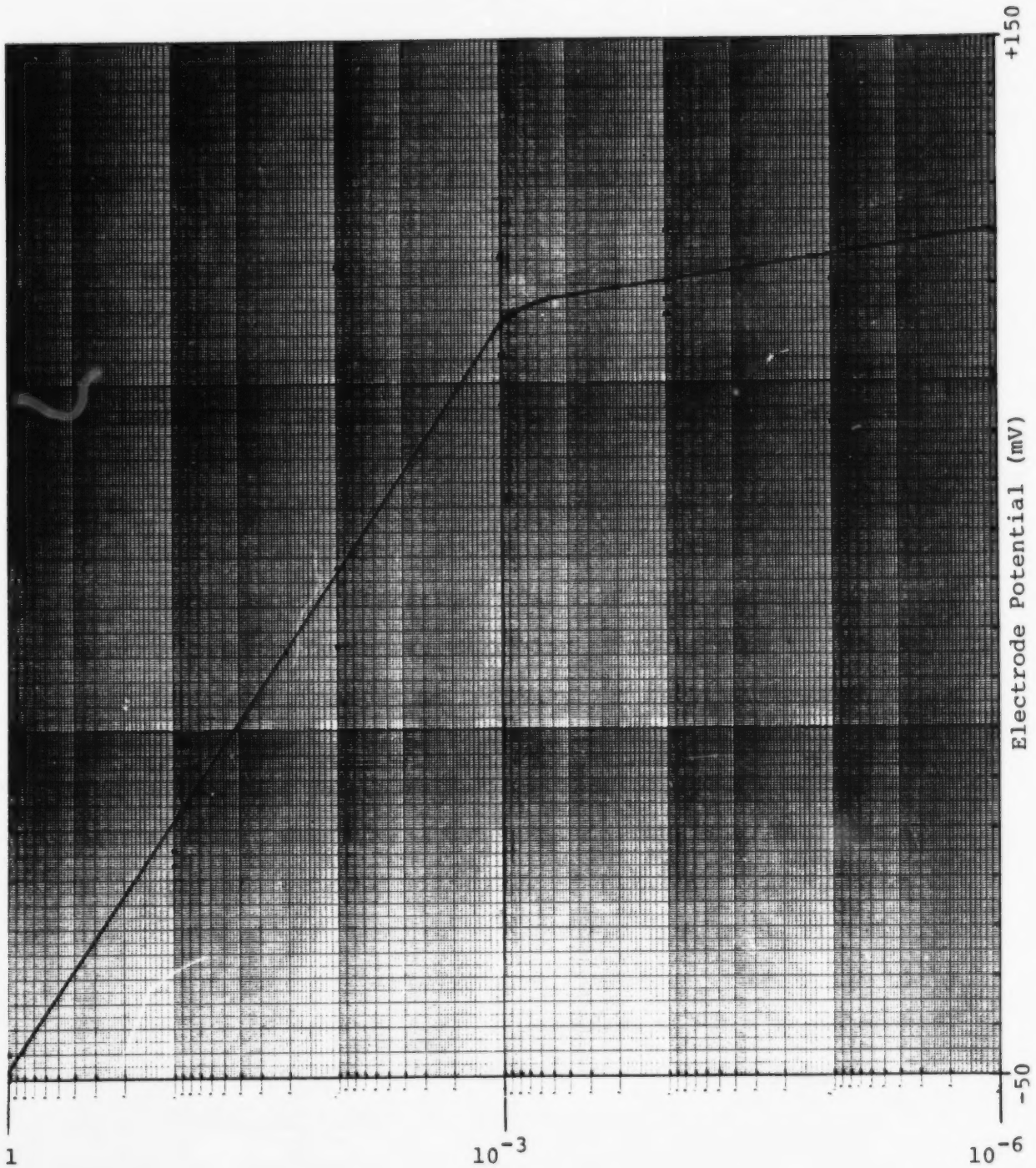

Figure 1. Calibration Curve for the Nitrate Specific Ion Electrode

of sulfuric acid. The concentrations of the sulfate ions in these standard solutions were selected so that they contained the amounts of sulfate ion that we expected to have in the mine samples, i.e., the concentrations were determined from the sulfate levels reported by Kirk and Seymour (6). The best titration curves, i.e., with the largest and sharpest change at the end point, were obtained when the lead perchlorate solution was 2.50×10^{-3}M. When more or less concentrated lead solutions were used, there were smaller and less distinct changes in the electrode potential at the endpoint of the titration.

Once the concentration of the lead perchlorate solution had been established, we attempted to vary the experimental conditions to determine exactly how the titration should be done. This study was undertaken because the method used by Kirk and Seymour differed from that recommended by the electrode manufacturer. In the recommended method, the titration was done in a methanol-formaldehyde-water solution containing 2 ml of an ionic strength adjustor (ISA) solution. Kirk and Seymour on the other hand, did the titration in the methanol and water and did not use any ISA solution. An examination of the titration curves obtained when several standard solutions were titrated in the two different solvents and with and without ISA solution, showed that the titration curves were much better when the sulfate ion was titrated using the method

devised by Kirk and Seymour. Typical titration curves for samples containing fairly large concentrations (2.70×10^{-4} moles/liter) of sulfate ion are shown in Figure 2. As a result, all of the sulfate ion samples were titrated using Kirk and Seymour's method. This had the added advantage that our results could be compared with those reported by Kirk and Seymour.

Although the best procedure for titrating the sample had been chosen, the endpoint was often difficult to detect, particularly when the sulfate ion concentration was low. We weren't satisfied that we could determine the endpoint accurately and thus we investigated two other methods for finding the endpoint of the titration. One technique was to use a computer program to detect the point of inflection in the titration curve obtained by plotting the first derivative of the electrode potential against the volume of 2.50×10^{-3}M lead perchlorate solution that had been added to the sample. Unfortunately, this method was not as accurate or reproducible as the graphical method. In addition, this method was more time consuming than the graphical method and it was discarded.

The second approach was to determine the endpoint using the Gran's plot method, i.e., plotting the log of the electrode potential against the volume of 2.50×10^{-3}M lead perchlorate solution that had been added to the sample. The results obtained when the data was plotted in this manner did not make

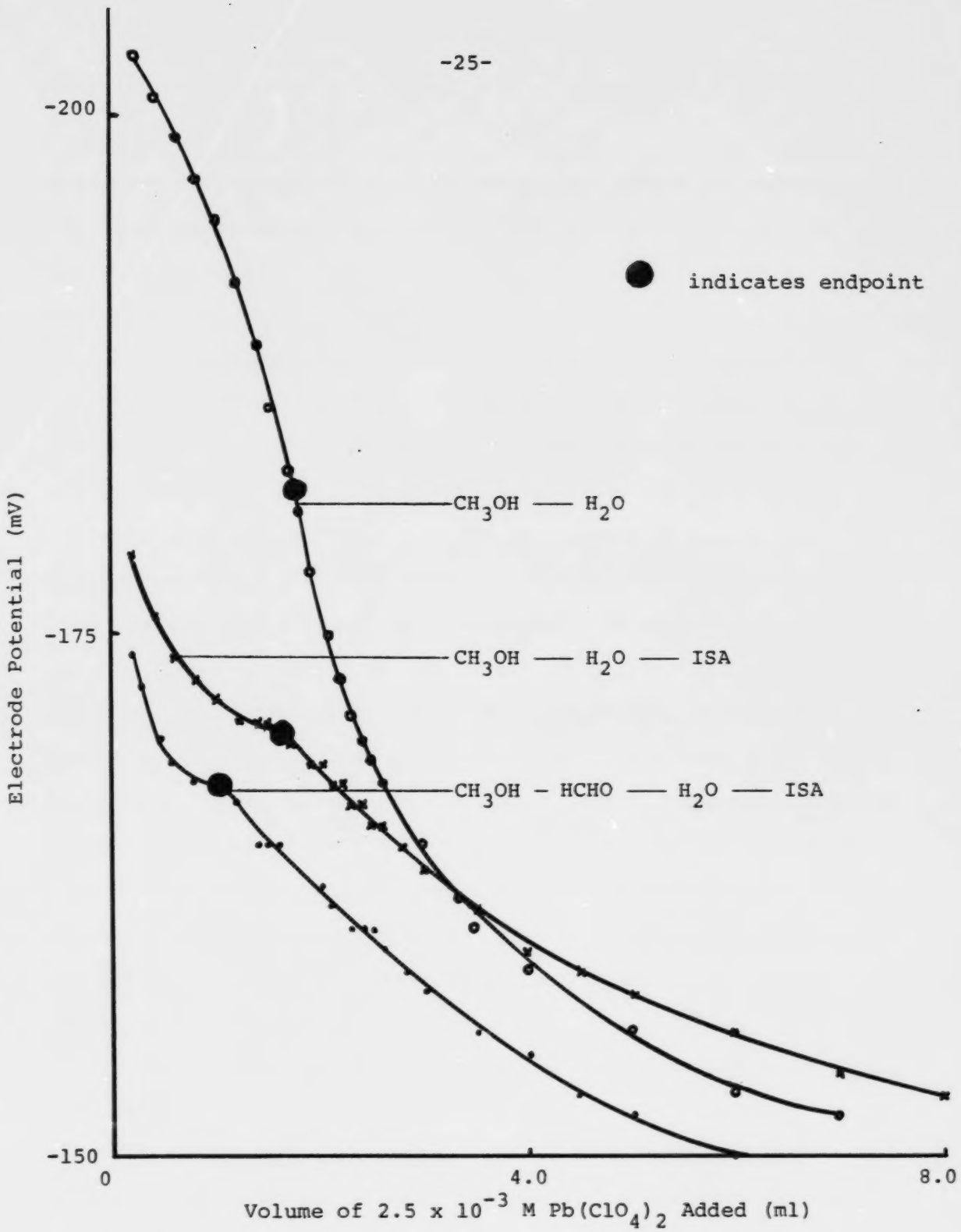

Figure 2. Titration curves for 10 ml of a 2.70×10^{-4} molar sulfuric acid solution.

any sense at all. The source of the problem was eventually traced to the fact that the end point and the shape of the titration curve depend on the pH of the solution, i.e., the end point of sodium sulfate solutions and sulfuric acid solutions containing equal amounts of sulfate ion were different. Since we were attempting to determine the concentration of sulfuric acid on the filters collected underground, the acidity of each sample would be different. This meant that the Gran's plot method would not work on our samples and this approach was also dropped.

U. V. method:-The failure to find a better method of determining the end point from the titration curves meant that it would be difficult to find the end point when we were titrating mine samples. As a result, we decided to look for another method for analyzing sulfate ions (sulfuric acid). A spectrophotometric technique has been widely used to determine the concentration of sulfate ions (sulfuric acid) in aqueous solutions (9). In this analysis, barium chloride crystals are added to the sample and the sulfate ions are converted into insoluble barium sulfate, equation 4.

$$BaCl_2 + SO_4^{=} \longrightarrow BaSO_4\downarrow + 2Cl^{-} \qquad [4]$$

The barium sulfate precipitate exists as a stable suspension for several minutes and since the turbidity caused by the precipitate is linearly related to the amount of barium sulfate and thus to the amount of sulfate ion in the sample, one can

determine the amount of sulfate ion in the sample by measuring the fraction or amount of visible (420 nm) radiation that is absorbed (scattered or reflected) by the precipitate in a spectrophotometer.

This method was attractive because there are very few substances which interfere with the analysis, the results are independent of pH and the method is faster and easier than the titrimetric method. The only difficulty was that the particutate and the filter would have to be removed from the sample before the barium chloride crystals were added to the sample. This did not constitute a problem because we could stir (break up) the filter in 10.00 ml of deionized-double distilled water and then remove the glass fibers and particulate by filtering the solution. The beaker and funnel could be rinsed with an additional 15 ml of water and then the barium chloride crystals could be added to the 25 ml sample and the absorbance at 420 nm measured. Thus, it appeared that the method could be adapted to the analysis of mine samples and since the method was attractive for other reasons, we spent some time investigating this procedure.

Although the spectrophotometric method worked well on known standards, we did not know whether the method gave accurate results when it was applied to mine samples. We attempted to determine whether the spectrophotometric method could be used on mine samples by comparing the results from the

titrimetric and/or by the spectrophotometric analysis of samples collected simultaneously in the same location in a mine, i.e., some samples were titrated and then analyzed by the spectrophotometric technique. In other experiments, samples were analyzed by only one of the two methods so that the results on identical samples could be compared. In fact, the results from both series of experiments suggest that the u.v. method can be used to determine the sulfate ion concentration on the filters collected in the underground mine. The results of these comparison tests are discussed below.

The results of the sulfate analysis of individual filters, midget impinger samples and the support disc portion of the filter holders are given in Table 6. The average concentrations of sulfate ion found by each method are also presented in Table 6. An examination of the individual analyses as well as the average concentrations shows that most of the results obtained by the titrimetric and the spectrophotometric methods are in good agreement. Moreover, the agreement is observed whether one is analyzing samples collected on filters, in midget impingers or even on the support discs from the filter holder. In fact, only 9 of the 49 results (18%) have not been included in calculating the averages in the last column of Table 6 and in Table 7. Although this number seems high, we do not believe that it is too high when one considers that all of these results were obtained while we were learning the

Table 6. Sulfate ion concentration in samples analyzed by the titrimetric and/or spectrophotometric method.

Samples	mg/m^3 Sulfate Ion as Determined Using the Titrimetric Method/Spectrophotometric Method[a]									Average Titrimetric Method / Spectrophotometric Method
Filters from the 25-29-30 stope	2.25[b] / 0.28	0.30 / 0.43	0.0[b] / 0.18	0.0[b] / 0.57	0.19 / 0.27	0.48 / 0.43	0.13 / 0.39	0.19 / 0.99[b]	____ / 0.20[c]	0.26 / 0.34 = 0.76
Filters from the 26-31-34 stope		0.04 / 0.08	0.13 / ____	____ / 0.26	0.27 / 0.03[b]	0.32 / 0.03[b]	0.18 / 0.03[b]			0.18 / 0.17 = 1.06
Midget Impingers	1.05 / 0.75	____ / 0.67	1.10 / 0.13[b]	____ / 0.92	0.59 / 0.88	____ / 1.44	1.83 / 0.01[b]	0.63 / 0.35	____ / 0.32	1.04 / 0.76 = 1.37
Support discs from filters	0.12 / 0.17	____ / 0.08	____ / 0.17	0.07 / 0.17						0.10 / 0.15 = 0.67
								average		0.97/1.00

a. In the case where two values are given for a sample, the spectrophotometric analysis was carried out on the solution analyzed titrimetrically.

b. Not used in calculating the averages in Tables 6 and 7.

c. Analyzed at Inco Metals Company, Copper Cliff Laboratory.

Table 7. The average sulfate ion in samples analyzed by the titrimetric and/or spectrophotometric method.

Samples	Average Concentration of Sulfate Ion in mg/m^3					
	Titrimetric Method	Spectrophotometric Method Only	Spectrophotometric Method After the Titrimetric Method	Total Spectrophotometric Method	$\frac{\text{Titrimetric}}{\text{Spectrophotometric only}}$	$\frac{\text{Titrimetric}}{\text{Total Spectrophotometric}}$
Filters from 25-29-30 stope	0.26	0.20	0.36	0.34	$\frac{0.26}{0.20} = 1.30$	$\frac{0.26}{0.34} = 0.76$
Filters From 26-31-34 stope	0.18	0.26	0.08	0.17	$\frac{0.18}{0.26} = 0.69$	$\frac{0.18}{0.17} = 1.06$
Midget Impinger	1.04	0.84	0.66	0.76	$\frac{1.04}{0.84} = 1.24$	$\frac{1.04}{0.76} = 1.37$
Support Discs from filter	0.10	0.13	0.17	0.15	$\frac{0.10}{0.13} = 0.77$	$\frac{0.10}{0.15} = 0.67$
Average $\frac{\text{Titrimetric}}{\text{Spectrophotometric}}$					$\frac{1.00}{1.00}$	$\frac{0.97}{1.00}$

analytical techniques. Of the nine results that were discarded, three were obtained using the titrimetric method and two of these results were for Gelman filters which required less titrant than a blank (unused filter). The other titrimetric result that was discarded was the extremely high value (2.25 mg/m^3) that was found on the first mine filter we ever analyzed. This value was discarded beacause it was more than 14 standard deviations away from the mean for the first set of filters.

The other six results that were discarded when we calculated the averages were from spectroscopic analyses performed on samples that had already been analyzed titrimetrically. Five of these samples were discarded because the absorbances of the barium sulfate solutions were equal to or less than those of the blank, i.e., the absorbance found when deionized-double distilled water was filtered and analyzed spectrophotometrically. In fact, it is not surprising that a number of the results obtained spectrophotometrically after the titrimetric analysis are too low (effectively zero) because it is very easy to lose the sulfate ion in the four extra steps that were required between the titrimetric and spectrophotometric analyses. These steps were:

i) removal of the methanol under reduced pressure on a rotary evaporator (the methanol was removed so that the lead sulfate precipitate formed in the titrimetric analysis would redissolve)

ii) heating the remaining solution to increase the solubility of the lead sulfate, i.e., to try to ensure that all of the sulfate ion was in solution

iii) filtering the hot solution to remove the glass fibers of the filter and any particulate (hopefully the sulfate ion is in solution at this stage and passes through the filter)

iv) rinse all the apparatus with deionized-double distilled water so that the recovery of sulfate ion is quantitative.

Sulfate ion could be lost in any of these four steps although it is more probable that the sulfate was lost because the methanol was not completely removed from the sample before it was filtered. If this were the case, the lead sulfate would not be soluble and would be lost in the filtration step. The other sample that was not included in calculating the averages was collected on a Gelman filter. This sample was discarded because the amount of sulfate found in the spectrophotometric analysis was almost 5 standard deviations from the mean. Finally, it is interesting to note that 3 of the nine results that were discarded were from samples collected on Gelman filters and only five of the eight, or 63%, of the sulfate analyses of the samples collected on Gelman filters were used in calculating the average values in Tables 6 and 7. This certainly confirms that the Whatman filters are the best filters for collecting samples in dieselized underground mines.

An examination of the average results in Table 6

indicates that the two methods give comparable results. For example, the ratio of the titrimetric to spectrophotometric results are 0.76 for the first set of filters, 1.06 for the second set of filters, 1.37 for the samples collected in the midget impingers and 0.67 for the support discs. The average ratio is 0.97. This certainly suggests that the two methods give the same results and that the scatter in the ratio is caused by a random experimental error. In any case, the maximum difference in the ratios is only 37% indicating that the analysis agree within 37%.

The reasonably good agreement of the results obtained by the two methods is confirmed by the averaged results in Table 7. For example, there is reasonably good agreement between the titrimetric analyses and the samples that were only analyzed spectrophotometrically, i.e., without first having been analyzed titrimetrically. This is shown by the ratios of the titrimetric to spectrophotometric only analyses: 1.30, 0.69, 1.24 and 0.77. The average ratio is 1.00. This suggests that the different ratios are due to random experimental error. Thus, the two methods again appear to give comparable results and it seems safe to conclude that either method for analyzing the sulfate ion in solution is acceptable.

Finally, the average results from the titrimetric analysis are compared i) with those obtained using the spectrophotometric method to analyze the sulfate ion recovered

from the titrimetric analysis and ii) with all of the spectrophotometric analyses. In all comparisons except one, the averages are in good agreement. The only large discrepancy is the value of 0.08 for the spectrophotometric analyses carried out after the titrimetric analysis of the filters collected in the 26-31-34 stope. Although this value is much lower than the titrimetric value of 0.18, the 0.08 mg/m^3 is based on the result of one filter and the single value is probably too low because some of the sulfate was lost in the four steps between the two methods of analysis. In all of the other cases, the agreement between the titrimetric and spectrophotometric methods of analysis is acceptable whether one compares the titrimetric results with the spectrophotometric only, the spectrophotometric obtained after the titrimetric or all of the spectrophotometric results. As a result, one could use either method for analyzing the sulfate ion in the mine samples. Since these two methods give equivalent results, we believe that it is better to use the spectrophotometric analysis for determining the concentration of sulfate ion in the mine samples because

i) it is faster than the titrimetric analysis

ii) it is easier experimentally

iii) the nitrate ion and pH analyses do not affect the spectrophotometric sulfate analysis whereas they do make it more difficult to detect the endpoint using the lead perchlorate titrimetric method. This presumably occurs because the

ionic solutions in the outer chamber of the pH and reference electrodes leak into the sample and have the same effect as an ISA solution, Figure 3.

iv) the spectrophotometric analyses are more reproducible, i.e., the standard deviations for the average results are slightly smaller for the spectrophotometric analysis. Moreover, even better reproducibility would be expected if the samples were only analyzed spectrophotometrically.

In conclusion, the spectrophotometric analysis for the sulfate ion has several advantages and we believe that this is the best method for analyzing the sulfate ion in the mine samples.

Sulfate Ion, Nitrate Ion and pH Concentrations in Dieselized Underground Mines

Sulfate Ion:-The sulfate ion concentrations found for the samples collected in two different stopes at Falconbridge Nickel Mines, Strathcona Mine are given in Table 8. We have included all the results, regardless of the method of analysis because the two methods give comparable results. This is in fact confirmed by the small standard deviations for the average sulfate concentrations (last column of Table 8). The filters collected in the 25-29-30 stope were collected simultaneously in one place approximately half way from the

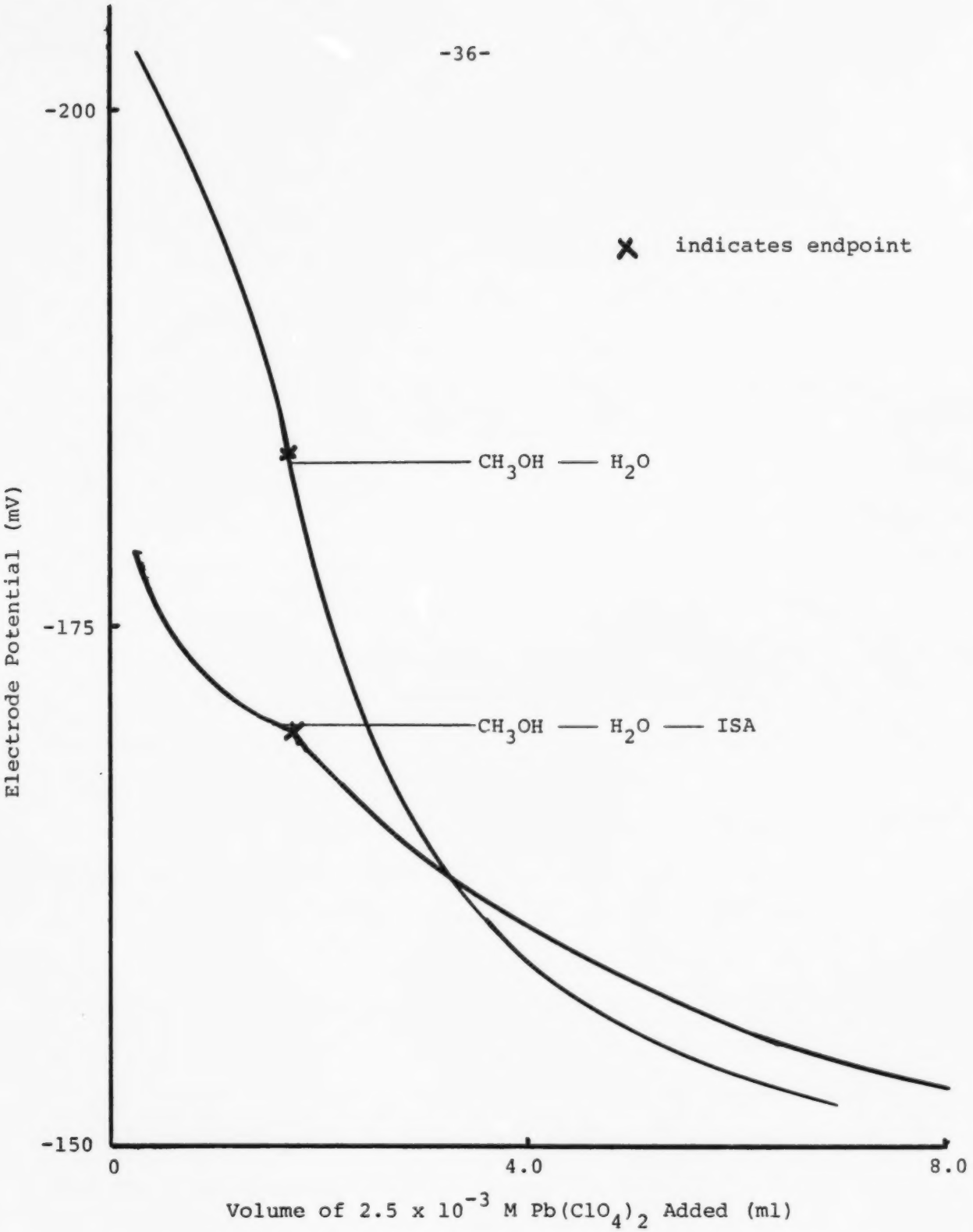

Figure 3. The effect of adding ionic strength adjustor (ISA) solution on the titration curve.

Table 8. The concentration of sulfate ions in samples collected in dieselized underground mines.

	Sulfate Ion Concentration in mg/m^3	Average
Filters collected in the 25-29-30 stope	0.30, 0.19, 0.48, 0.13, 0.19, 0.28, 0.43 0.57, 0.27, 0.43, 0.39, 0.20, 0.18	0.31 ± 0.14[a]
Filter support discs from samples collected in the 25-29-30 stope	0.08, 0.27, 0.13, 0.44, 0.15, 0.17	0.21 ± 0.13[a]
Filters collected in the 26-31-34 stope	0.04, 0.13, 0.27, 0.32, 0.18, 0.08, 0.26	0.18 ± 0.10[a]
Filter support discs from samples collected in the 26-31-34 stope	0.12, 0.07, 0.17, 0.08, 0.17, 0.17	0.13 ± 0.05[a]
Midget Impinger samples collected in the 26-31-34 stope	1.05, 1.10, 0.59, 0.75, 0.67, 0.92, 0.88, 1.44	0.93 ± 0.27[a]
Midget Impinger samples collected in series with (after) the filters collected in the 26-31-34 stope	1.83, 0.63, 0.35, 0.32, 0.86	0.80 ± 0.62[a]

[a] Standard deviation

muck pile and the dump site (about 50 feet). The samples were collected within 10 feet of the path taken by the diesel. The duty cycle took approximately one minute and ore was being mucked for approximately 105 minutes out of the 165 minute sampling time. The rest of the time the Deutz ST2, 78 Horsepower diesel fitted with a PTX catalytic converter, was idling. The ventilation in the stope was approximately 20,000 cfm. The sulfate ion concentration on the filters collected in the 25-29-30 stope was 0.31 mg/m^3 with a standard deviation of ± 0.14 mg/m^3.

In the 26-31-34 stope, the filters were collected approximately 20 feet from the dump site but within 10 feet of the path of the diesel, Figure 4. In this case, the duty cycle was approximately 1.5 minutes. Twelve thousand cfm of fresh air entered the stope near the muck pile and another 8,000 cfm of fresh air was added opposite the dump site. Thus the total ventilation in the stope was roughly 20,000 cfm.. The 78 Horsepower Deutz ST2 diesel fitted with a PTX catalytic converter was mucking ore for approximately 155 minutes out of the 190 minute sampling period. The remainder of the time the diesel was idling. The sulfate ion on the filters indicated that there was 0.18 mg/m^3 (standard deviation = ± 0.10 mg/m^3) of sulfate ion in the mine air at the sampling site. We believe that the lower concentration of sulfate ion was observed in this stope because the samples were collected near the dump site

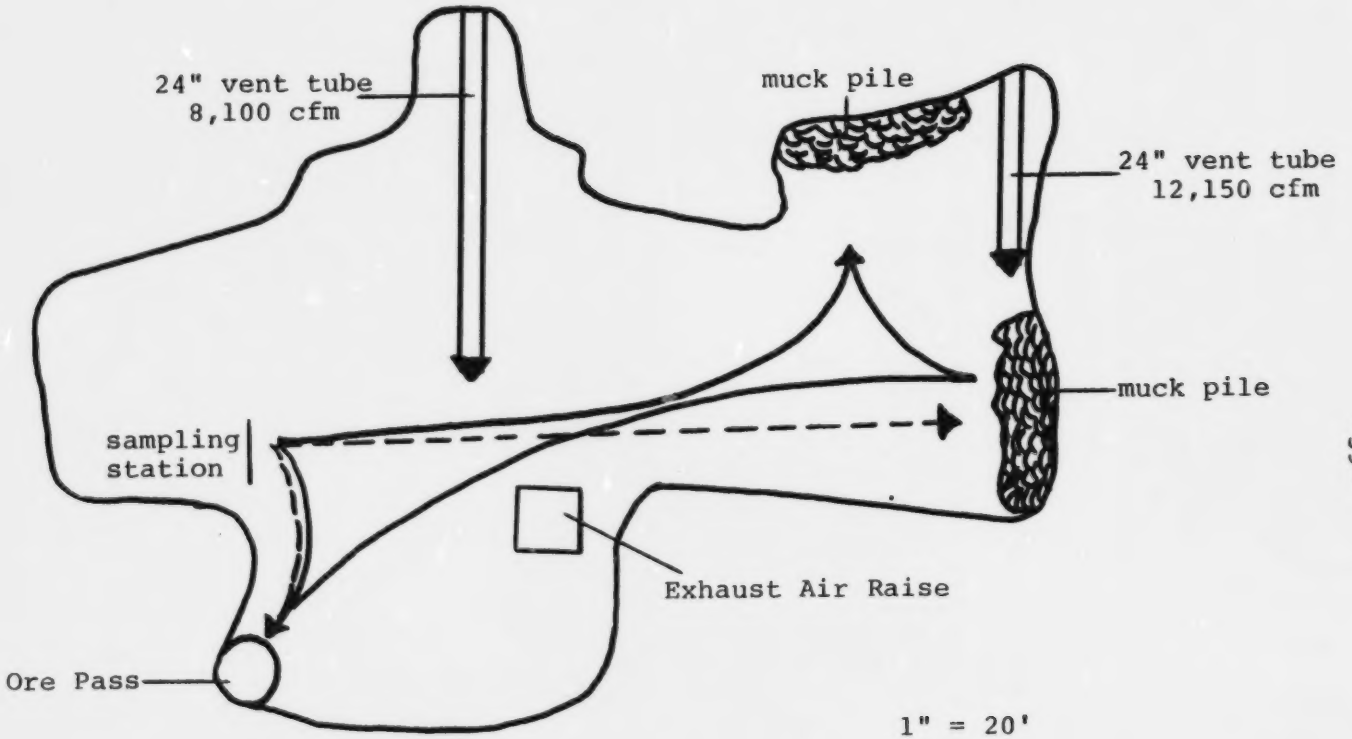

Figure 4. Level Plan 26-31-34 stope, Strathcona Mine, March 29, 1982.

(ore pass) and farther (approximately 80 feet) from the two muck piles. Lower sulfate emissions would be expected near the dump site because the diesel does not work hard when it is dumping. This is in fact what has been observed. The sulfate ion concentration was 0.31 mg/m^3 when the sample was collected 50 feet from the muck pile and only 0.18 mg/m^3 80 feet from the muck pile.

A comparison of the sulfate levels found in this study with those reported by other workers indicates that these levels are in the range expected. For example, Kirk and Seymour reported sulfate ion (sulfuric acid) concentrations ranging from 0.14 to 1.9 mg/m^3 in the air of an uranium mine at Elliot Lake, Ontario (6). Although our results (0.18 and 0.31 mg/m^3) are near the lower end of this range, both values are within the range found by Kirk and Seymour. The sulfate levels we observed are probably lower than those found by Kirk and Seymour because a smaller diesel (an ST2 versus an ST8) was used and the ventilation was much greater (approximately three times the maximum ventilation per break horsepower used in the Elliot Lake sampling).

Sharp (10) has measured the sulfate ion concentration in the raw exhaust from a Caterpillar 3304 PC-T turbocharged diesel operating with and without a PTX catalytic converter. The results showed that the sulfate ion concentrations were very different in the two experiments. When the diesel was

not fitted with a PTX converter, Sharp found 6.7 ± 0.3 mg/m^3 of sulfate ion in the untreated exhaust. When the PTX catalytic converter was used to treat the exhaust, the sulfate ion concentration was an average of 62 mg/m^3 in the raw exhaust. If we assume a dilution factor of between 30 and 100, the sulfate ion in a mine where the exhaust was not treated with a catalytic converter should be between 0.07 and 0.22 mg/m^3.. The sulfate ion in the diluted exhaust (mine air) when a diesel was fitted with a PTX catalytic converter would be expected to be between 0.6 and 2 mg/m^3.. Our values are near the top of the range expected for a diesel operating without a catalytic converter and are 1/3 to 1/2 of the values found for the PTX equipped Caterpillar diesel. However, the diesel used in the stope where our samples were obtained is smaller than the Caterpillar 3304 PC-T diesel used by Sharp and moreover, it is entirely possible that the dilution factor in our sampling was greater than 100. Another factor that would reduce the sulfate ion concentration is that the ventilation was approximately three times that required by law in the area where our samples were collected. This also would be expected to increase the dilution factor and decrease the concentration of sulfate ion in the mine environment significantly. All of these factors suggest that the sulfate ion concentrations that we have found are reasonable.

The concentrations of the sulfate ion in the 25-29-30

and 26-31-34 stopes can be compared with those reported by Kirk and Seymour in other ways. For example, these workers reported that the respirable dust samples had 0.80 ± 0.29 or 80% of the sulfate ion (sulfuric acid) found in the total dust samples and concluded that most of the sulfate was on the respirable sized particulate emitted from the diesel (6). In this study, both respirable and total dust samples were collected in the 25-29-30 stope. The results, Table 9, show that the sulfate ion was equally concentrated in the respirable dust and the total dust samples, i.e., the sulfate ion concentration was 0.32 ± 0.15 mg/m^3 in the respirable dust samples and 0.30 ± 0.13 mg/m^3 in the total dust samples. Since these two values are well within experimental error, it can be concluded that all of the sulfate ion is associated with the respirable sized particulate. This undoubtedly means that the sulfate is generated in the exhaust system and is absorbed on the particulate in the diesel exhaust. This conclusion seems likely because the diesel particulate is almost completely respirable (4). Although this finding is somewhat different than that of Kirk and Seymour, it is worth noting that the sulfate in the respirable dust samples was between 90 and 110 percent of the sulfate in the total dust samples in 11 of the 19 comparisons done by Kirk and Seymour. As a result, we do not believe that there is a major difference between the results obtained in the studies conducted in the nickel and the uranium

Table 9. The sulfate ion in the respirable and total dust samples collected on filters in the 25-29-30 stope, Strathcona Mine

Filters	Sulfate ion in mg/m^3	Average Sulfate ion in mg/m^3
Respirable	0.19, 0.30, 0.27, 0.43, 0.18, 0.57	0.32 ± 0.15[a]
Total Dust	0.28, 0.43, 0.48, 0.13, 0.19, 0.20, 0.39	0.30 ± 0.13[a]

a. Standard deviation

mines.

Kirk and Seymour (6) found that 0.53 ± 0.20 or 53% of the weight loss found in the respirable combustible dust (RCD) experiment could be accounted for if one assumed that all of the sulfate in the respirable dust samples was present as sulfuric acid and that the sulfuric acid was lost when the respirable dust samples were heated for 1 hour at 400°C in the RCD analysis. The analysis of the two RCD samples collected on silver membrane filters in the 26-31-34 stope showed that the respirable combustible dust was 1.05 and 1.02 or 1.04 ± 0.02 mg/m^3.. This, like the sulfate levels in this stope, is toward the lower end of the range found in the uranium mine by Kirk and Seymour, i.e., these workers found RCDs ranging from 0.8 to 3.0 mg/m^3..

Although both the RCDs and sulfates are in the range found by Kirk and Seymour, the sulfate in the 26-31-34 stope (0.18 mg/m^3) only accounts for 17 percent of the weight loss that occurred when the RCD samples were heated to 400°C. Although we do not know why the sulfate accounts for such a small portion of the RCD weight loss in our samples, two obvious sources that might account for the observed difference are the sulfur content of the fuel or a different efficiency of the catalytic converter on the smaller ST2 diesel used in this study. Unfortunately, we do not know which, if either, of these suggestions is correct.

One unexpected finding was that there are significant amounts of sulfate ion on the plastic discs that supported the fiberglass filters in the filter holder. In fact, the results in Table 8 show that the sulfate ion on the support discs is equal to 68% and 72% (an average of 70%) of the sulfate found on the filters collected in the 25-29-30 stope and the 26-31-34 stope, respectively. Although we do not know why a significant amount of sulfate is found on the discs, one possibility is that gaseous sulfur dioxide passes through the particulate on the filter, dissolves in some moisture on the filter holder and is then oxidized to sulfate ion, as air (oxygen) is drawn through the filter. If this is true, the sulfate found on the discs is merely a sampling artifact and does not mean that there is an error in the sulfate ion analysis of the mine samples. Although this rationale for the sulfate ion on the support discs cannot be proven, it seems reasonable because whatever is found on the discs would have to have passed through the glass fiber filter. Since the glass fiber filters remove even submicron particles quantitatively, it seems highly unlikely that any particulate or aerosol would pass through the glass fiber filter. This would be especially unlikely after some particulate had been collected on the filter. Thus, the sulfate must come from a gaseous material, most probably sulfur dioxide. Sulfur dioxide seems the most likely substance because SO_3 should react so rapidly with water on the

particulate and or filter that it would form sulfuric acid before it could pass through the filter.

The above hypothesis is consistent with the results we obtained when mine air samples were collected in midget impingers containing 20 ml of deionized-double distilled water. These samples were collected in midget impingers because we were concerned that the pH of the samples that we were collecting was incorrect and we wanted to try another method of collecting the samples in order to ensure that we were not looking at a sampling artifact when we measured the pH of a filter. In fact, four samples were collected in midget impingers at the sampling station in the 26-31-34 stope. In addition, two other samples were collected on filters that were followed by midget impingers containing 20 ml of deionized-double distilled water. This was done to determine whether all of the sulfate ion was collected on the filter.

Very high concentrations of sulfate ion were observed, Table 8, when the impingers were analyzed for sulfate ion. In fact, the samples collected in the impingers had an average of 0.93 ± 0.27 mg/m^3 of sulfate ion. This is 5.2 times the sulfate ion found on the filters in the 26-31-34 stope. High concentration of sulfate ion (0.80 ± 0.62 mg/m^3 or 4.4 times the sulfate ion found on the filters) were even found in the midget impingers that were in series (after) the filters in the sampling train. The large amounts of sulfate ion in the impinger after the filter

indicates again that some sulfur containing gas (probably sulfur dioxide) must pass through the filter, dissolve in the water in the impinger and then oxidize to sulfate ion when more air (oxygen) is drawn through the solution in the impinger. If this hypothesis is correct, only a small amount of the sulfur dioxide in the exhaust is converted into sulfur trioxide (sulfuric acid) by the PTX catalytic converter on the Deutz ST2 used in these tests. We do not know if this is reasonable because Lawson et. al. (11) has reported that 50% of the sulfur dioxide is oxidized to sulfuric acid in a PTX catalyst. The sulfate ion is even more concentrated in the samples collected in the impingers, i.e., it is 0.93 mg/m^3 rather than the 0.80 mg/m^3 found in the impinger after the filter. We believe that the impinger samples contain all the sulfate ion on the particulate and all of the sulfate formed from the SO_2 in the impinger. In fact, the sulfate ion in the impinger (0.98 mg/m^3) is almost equal to the sum of the sulfate on the filter (0.18 mg/m^3) and the sulfate in the impinger in series with the filter (0.80 mg/m^3). The close agreement between the sum of the sulfate ion in the filter and the impinger, and that found in the impinger samples, indicates that the results are reliable.

Nitrate Ion:-As stated previously, the analysis for nitrate ion did not go as well as we would have liked. The major problem was that the nitrate specific ion electrode was not particularly

stable. As a result, the analyses did not give consistent results, Table 10. In spite of the inconsistencies in the results, it would appear that the nitrate ion is present in very low concentrations in the mine environment. In fact, 20 of 27 or 74% of the analyses indicated that the nitrate ion was present at less than 0.1 mg/m^3.. The other 7 analyses gave values which were from ten to forty times the highest value (0.094 mg/m^3) found in the other filters. We believe, but cannot prove, that the high concentrations are incorrect. The only results that are interesting are the first two results in Table 8. These results suggest that there may be much more nitrate ion in the total dust sample than in the respirable dust sample. This implies that the nitrate ion is associated with the mine dust rather than the respirable diesel particulate. We suspect the nitrate ion comes from the explosive.

pH Analysis:-The results of the pH analyses were surprising. Three groups have analyzed undiluted and diluted exhaust samples for sulfate ion (6,10,11). Significant quantities of sulfate ion have been found in the exhaust and it has always been assumed that the sulfate ion was present as sulfuric acid. This has led to the concern for the miners because the TLV for sulfuric acid is only 1 mg/m^3 and the sulfate ion levels often exceed this in the mine.

Our pH analyses of the glass fiber filters, the samples

Table 10. Nitrate ion concentration in samples collected in Strathcona Mine.

Sample	Nitrate ion in mg/m^3	Average mg/m^3
Respirable Dust filters 25-29-30 stope	0.007,0.001, 0.002, 0.004	0.004 ± 0.003[a]
Total Dust filters 25-29-30 stope	1.88, 0.004, 0.094[b], 0.001, 0.88	0.57 ± 0.82[a]
Total Dust filters 26-31-34 stope	1.08, 0.002, 0.002	0.36 ± 0.62[a]
Support Discs 25-29-30 stope	0.002, 2.34, 0.001, 0.004, 0.001	0.47 ± 1.05[a]
Support Discs 26-31-34 stope	3.86, 0.002, 2.27, 0.002, 1.19	1.46 ± 1.64[a]
Midget Impingers	0.003, 0.004, 0.002, 0.002, 0.002	<0.003 ± 0.001[a]

a. Standard deviation
b. Analyzed using another method by Inco Metals Company, Copper Cliff, Ont.

collected in midget impingers and the support discs from the filter holders, Table 11, has shown that the pH of the samples (mine air) is much higher than we had expected. For example, blanks (the solution obtained when a Whatman GF/A filter was broken up in 10.00 ml of deionized-double distilled water) had a pH of 7.05 (see Table 2) and are effectively neutral. This meant that the filters were basic because the deionized-double distilled water used in all of these analyses had a pH=5.6±0.21. Since the solution containing the filters were neutral, the amount of acid extracted from the filter was directly related to the pH of the solution. The results from the pH analyses of the filters collected underground are given in the first two rows of Table 11. The average pH of the filters collected in the 25-29-30 stope was 6.74 $\pm$ 0.26 and thus the 10 ml solutions had an average of 1.82×10^{-7} moles/liter of hydrogen ion. The filters collected in the 26-31-34 stope had a slightly higher pH=6.96 and even less hydrogen ions. The hydrogen ion concentration in the 10 ml solutions containing these filters was only 1.10×10^{-7} moles/liter. If all of the sulfate ion found on these filters was present as sulfuric acid, the average pH of the 10 ml solution should have been 3.6 $\pm$ 0.3 for the filters collected in the 25-29-30 stope and 4.1 $\pm$ 0.3 for the filters collected in the 26-31-34 stope. Although the filters are slightly acidic, (blank (unused) filters in 10.00 ml of deionized-double distilled water have a pH of 7.05 or are neutral),

Table 11. pH of samples collected in Strathcona Mine

Sample	pH Found/pH Expected ($SO_4^=$)[a]	Average pH found / pH Expected ($SO_4^=$)[b]
Filters from 25-29-30 stope	$\frac{6.81}{3.8}$, $\frac{6.65}{4.0}$, $\frac{6.82}{3.3}$, $\frac{7.23}{3.2}$, $\frac{6.38}{3.4}$, $\frac{6.73}{3.8}$, $\frac{6.59}{3.9}$	$\frac{6.74\pm0.26}{3.6\pm0.32}$
Filters from 26-31-34 stope	$\frac{7.03}{3.7}$, $\frac{7.12}{4.2}$, $\frac{7.11}{4.2}$, $\frac{6.97}{3.7}$, $\frac{6.53}{4.6}$, $\frac{7.01}{4.0}$	$\frac{6.96\pm0.22}{4.1\pm0.34}$
Midget Impingers 26-31-34 stope	$\frac{7.16}{3.5}$, $\frac{7.12}{3.9}$, $\frac{8.09}{3.0}$, $\frac{7.82}{4.2}$, $\frac{7.51}{3.7}$,	$\frac{7.54\pm0.42}{3.7\pm0.45}$
Support discs from 25-29-30 stope	$\frac{4.83}{4.2}$, $\frac{6.05}{3.7}$, $\frac{6.29}{3.9}$, $\frac{6.08}{3.8}$, $\frac{5.57}{3.8}$, $\frac{6.10}{4.0}$	$\frac{5.82\pm0.54}{3.9\pm0.18}$
Support discs from 26-31-34 stope	$\frac{6.62}{4.2}$, $\frac{5.29}{-}$, $\frac{5.72}{3.90}$, $\frac{5.82}{4.0}$, $\frac{5.66}{3.9}$,	$\frac{5.82\pm0.49}{4.0\pm0.14}$

a. The pH of the deionized-double distilled water used in these analyses was 5.63±0.24

b. The error limits are the standard deviation

the amount of acid is much lower than one would have found if all of the sulfate ion were present as sulfuric acid. In fact, the pH analysis shows that only 0.07% and 0.14% of the sulfate ion on the filters is present as sulfuric acid.

The same phenomenon was observed when we measured the pH of the samples collected in midget impingers in the 26-31-34 stope. These samples, row 3, Table 11, had an average pH of 7.54 ± 0.42. Since these samples were collected in 20.00 ml of deionized-double distilled water that was acidic, i.e., had a pH of 5.63 ± 0.21, the mine air drawn through the impinger must have been quite basic and neutralized (consumed) all of the acid in the water. The fact that the impinger samples were so basic was particularly surprising because the high sulfate ion concentrations found in the impinger samples, Table 8, were thought to arise because sulfur dioxide was oxidized (converted) into sulfuric acid in the impinger. If this occurred, the pH of the impinger sample should have been low. In fact, if all the sulfate was present as sulfuric acid, the pH of the impinger sample would have been 3.7 ± 0.45.

Since the conversion of sulfur dioxide into sulfuric acid occurred in the impinger, the high pH could only be found if the mine air contained some basic material that could react with (neutralize) the sulfuric acid generated in the impinger. The average pH of the samples obtained from the impingers that were in series (after) the filters in the sampling system was

also high (7.67 ± 0.16). This means that the basic material passes through the filter, and thus this substance must be a gas. After this gas passes through the filter, it dissolves in the water in the impinger and reacts with the sulfuric acid. The only problem that remains is to identify the basic gas.

One possibility is that the basic gas is ammonia. Ammonia is generated in the blasting operation and is often trapped in the open spaces in the muck pile. This gas would be released when the ore is moved in the mucking and dumping operation and could have been drawn into the samplers. The ammonia could react with the sulfuric acid on the particulate on the filter or on the support disc converting the sulfuric acid into sulfate ion, equation 5.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \qquad [5]$$

Ammonia is extremely soluble in water and would dissolve in the water in the impinger where it would neutralize the sulfuric acid in the impinger. Unfortunately, we did not think of this possibility in time to analyze the impinger samples for ammonium ion and thus do not know whether this explanation is reasonable.

Finally, the pH of the support disc from the filter holders used to collect the samples in the 25-29-30 stope and the 26-31-34 stope was 5.82 ± 0.5. These samples are also basic although not nearly as basic as the impinger samples, i.e., the pH of the sample is roughly 0.20 pH units more basic

than the deionized-double distilled water that was used in the analysis. Again, if the sulfate ion on the discs was formed from the sulfur dioxide that passed through the filter and dissolved in the water on the support disc, the discs should have been acidic with a pH of approximately 4.0. The higher pH of the solution again suggests that some basic gas (perhaps ammonia) has passed through the filter and neutralized the sulfuric acid on the discs.

An alternative explanation for the high pH is that the sulfate ion that we detected never existed as sulfuric acid but was all inorganic sulfates. This could be possible because inorganic sulfates are present in the mine atmosphere. For example, the typical sulfate ion concentration in the water used in Strathcona Mine is approximately 650 ppm.. Since this water has a pH of greater than 7,i.e., is basic, the sulfate must be present as inorganic salts. If small droplets of water were drawn onto the filter where it evaporated depositing inorganic sulfates on the filter, or into the midget impinger, sulfate ions would be detected in our analysis and the sample would not be acidic.

Another possible source of neutral sulfate ion is the mine dust. Metallic sulfides in the ore can be oxidized to metallic sulfates, e.g., iron sulfate or nickel sulfate, etc., and if a significant amount of this dust was collected, we would find high concentrations of sulfate ion but the sample

would not be acidic.

Although this source of sulfate ion is possible, it seems unlikely for several reasons. First, the oxidation of the ore is slow, i.e., it takes at least five days for a noticeable amount of oxidation to occur (12). Thus, it is unlikely that a significant amount of the sulfides in the ore would have been oxidized to sulfates in the 16 hours between the blasting and mucking operations. Moreover, this oxidation is even more unlikely if ammonia fills the holes in the muck pile. In addition, an RCD sample was analyzed for nickel and iron so that we could estimate how much of the sulfate ion could be accounted for if one assumed that the iron and nickel was all in the sulfate form. The two RCD samples had 0.002 mg of nickel and 0.08 ± 0.02 mg of iron. If the iron were all $Fe_2(SO_4)_3$ and the nickel were all $NiSO_4$, these salts would account for between 3 and 50 percent of the sulfate found in our samples[1]. Thus, the metallic sulfate can only account for a portion of the sulfate found on the filters collected in the mine. The sulfate ion is all found on respirable sized particles, and it is highly unlikely that the mine dust would all be respirable. For all these reasons, we have concluded that mine dust does not contribute a significant portion of the sulfate ions.

Finally, we know that sulfate ion is generated by catalytic converters (10,11) and this sulfate has to be present

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[1]The filters we collected had between 0.04 and 0.88 mg of sulfate. The iron and nickel sulfate would contain 0.02 mg of sulfate.

in some form in the mine air. Moreover, diesel exhaust is almost completely respirable (4) and thus the sulfate ion in the diesel exhaust would be on respirable sized particulate. Since all of the sulfate is on respirable sized particles and, moreover, is towards the lower end of the range of sulfate ion concentrations one would expect from a diesel engine fitted with a PTX catalyst, all or almost all of the sulfate ion on the filters must have been generated in the exhaust system (PTX catalytic converter) and little or none of the sulfate is from mine dust or water aerosols in the mine air.

If the sulfate ion was produced as sulfuric acid in the exhaust system, one must conclude that the sulfuric acid is neutralized rapidly and that the sulfuric acid concentration is probably very low in the mine air. Unfortunately, we have not analyzed enough samples from different types of mines or mine environments to know whether our results are representative of the whole industry. If these results are typical and the pH of the mine air is high, the concern that miners are exposed to high concentrations (greater than 1 mg/m^3) of sulfuric acid is not warranted.

CONCLUSIONS AND RECOMMENDATIONS

A procedure for analyzing glass fiber filter and midget impinger samples collected in dieselized underground mines for sulfate ion, nitrate ion and pH has been developed. Although we do not have total confidence in the analysis for nitrate ion, we believe the results of the sulfate ion and pH analyses are accurate.

This study has shown that the Whatman GF/A glass fiber filters are the best filters for collecting underground samples because there is less oxidation of sulfur dioxide on the filter, the filter has smaller concentrations of sulfate ion, i.e., the blanks are smaller, the filter is easier to handle experimentally, the results are more reproducible and the pH of the filter and deionized-double distilled water is effectively 7.00.

We have also developed a spectrophotometric procedure for determining the amount of sulfate ion in the mine samples. This new method is better than the lead specific electrode method because it is faster and easier to use than the specific ion electrode method and because it is more compatible with the pH and nitrate ion analyses that were done on the filters. Because we have found that the two methods for analyzing the sulfate ion are identical within experimental error, we believe that the sulfate ion analyses should be done spectrophotometrically.

Thus we recommend collecting underground samples for sulfate ion, nitrate ion and pH analyses on Whatman GF/A filters. The spectrophotometric method should be used to determine the amount of sulfate ion. The analysis for nitrate ion needs to be improved. Unfortunately, time did not allow us to develop a better procedure.

This study has confirmed that sulfate ion is present in the mine environment. The concentrations of sulfate ion in a well ventilated stope, i.e., with 20,000 cfm of ventilation in a stope where a 78 Horsepower Deutz ST2 diesel was mucking ore, were 0.31 and 0.18 mg/m^3.. Thus, the sulfuric acid concentration would be less than one third of the TLV concentration if all the sulfate ion were present as sulfuric acid. The pH analysis of samples collected using two different sampling methods showed that the mine air was not acidic, but basic. In fact, our calculations show that only approximately 0.1 percent of the sulfate ion is present as sulfuric acid. Thus, the sulfuric acid concentration is far below the TLV concentration in the mine environments we have tested and if these results are typical, the sulfuric acid in dieselized underground environments is not a problem from a health point of view. Unfortunately, we have only done our sampling in one mine and in one type of mining environment. Moreover, a small diesel engine was used in the stopes we tested and the ventilation was in excess of that required by law. If more sulfate were generated

by a larger diesel in a mine where the ventilation was lower, the sulfuric acid concentration might be much higher than we have found.

The basic gas (possibly ammonia) that we believe was present in the stopes where we sampled can also affect the sulfuric acid concentration in the mine air significantly. We obviously cannot reach a definitive conclusion about the health effects related to the sulfuric acid that is undoubtedly produced in the catalytic converter, until the basic substance(s) are identified and analyzed quantitatively. If these basic substances are not present in other mine environments, and if large diesels, e.g., an ST8, are used in areas where the ventilation is at the legal limit, miners may well be exposed to sulfuric acid levels in excess of the TLV.. Obviously, more testing in other mine environments is necessary before we can state whether sulfuric acid is a problem in underground mines. For example, worthwhile experiments would include collecting samples i) in an area where a diesel is not mucking and dumping, ii) very close to the exhaust outlet to learn whether the samples are acidic as they leave the engine, iii) in a dry mine environment where no vapour and/or sulfate ore would be found and iv) to test for ammonia in the mine environment.

The nitrate ion concentration appears to be very low, i.e., less than 0.1 mg/m^3 in underground mines although a few higher values were found on some of the total dust samples

collected on glass fiber filters. None of the respirable dust samples seem to have any nitrate ion suggesting that little or no nitric acid is associated with the diesel exhaust.

EXPERIMENTAL

The samples collected in a dieselized underground mine were obtained in two different ways, on filters and in midget impingers. In two cases, a midget impinger was used in series with a glass fiber filter. The samples were collected by drawing approximately two litres of mine air per minute through the filter and/or midget impinger with a personal sampler pump. The time of collection and the initial and final flow rates through each pump were recorded so that the volume of mine air sampled was known accurately. Each of these samples were analyzed for pH, for nitrate ion and for sulfate ion. Some of the samples were analyzed for sulfate ion using two different methods, i.e., using a lead specific ion electrode and a spectrophotometric method of analysis.

Sample Collection:

The samples on the glass fiber or spectrograde silica filters were collected on 25 mm filters mounted in polycarbonate Sartorius 25mm filter holders (Canlab number F2858-58) that had been modified in two ways. First, the top plastic filter support was removed so that the air could fall uniformly on the filter. The second modification involved drilling as many small holes as possible in the bottom plastic filter support so that the pump would pull

the air sample through the filter more evenly, Figure 5.

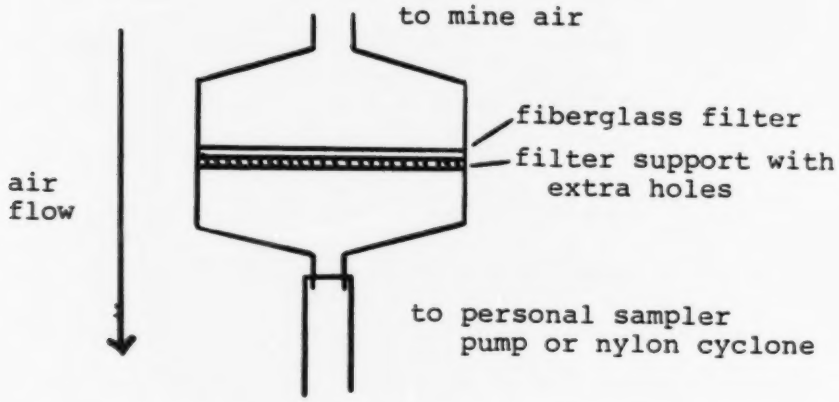

Figure 5. Polycarbonate filter holder used to collect dust samples

The filters were mounted in the filter holders in the lab. The filter holders were sealed (to keep the filter clean) by joining the rubber tube from the exit side of the filter holder to the intake side. The rubber tube was disconnected from the inlet port of the filter holder and connected to the personal sampler pump immediately before the sampling was begun. At the end of the sampling period, the filter holder was resealed by removing the rubber tube from the pump and putting it over the inlet port of the filter holder. This arrangement was maintained until the filter holder was opened and the filter analyzed. No special precautions were taken for storing the filters. They were simply kept in the lab at room temperature until they could be analyzed.

The midget impinger samples were collected by drawing mine air through the 20 ml of deionized-double distilled water that had been placed in the midget impinger. The 20 ml of deionized-double distilled water was placed in the impinger in the lab and then the impinger was closed by joining the rubber tube from the exit to the inlet tube of the impinger. The sample was collected by removing the rubber tube from the inlet port of the impinger and connecting it to the personal sampler pump. At the end of the sampling period, the impinger was resealed by removing the rubber hose from the pump and connecting it to the inlet port of the impinger. These samples were stored in this manner until the solution could be analyzed.

Sample Preparation:

In the cases where the samples were collected on filters, the solution that was analyzed was obtained by placing the filter, a magnetic stirring bar and 10 ml of deionized double distilled water[1] into a 100 ml plastic beaker. Then, the mixture was stirred until the filter had been broken up into individual glass fibers. This required less than 10 minutes when the samples were on Whatman GF/A type filters. When the Gelman spectrograde filters were used, the filters could not be broken apart by the stirrer and thus the filters were simply stirred (mixed) with the 10 ml of deionized-double distilled water for

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1. The 10 ml of deionized-double distilled water was added with a volumetric pipette.

approximately 10 min before the analyses were begun. The 10 ml solution obtained in this way was analyzed for pH, nitrate ion and sulfate ion.

For the samples collected in the midget impingers, the aliquots taken for analysis were obtained by diluting the solution in the midget impingers to 25 ml with deionized-double distilled water. Then, two, 10 ml samples were transferred into two different 100 ml plastic beakers using a 10 ml volumetric pipette. The analyses for pH, nitrate ion and sulfate were carried out on these 10 ml samples.

pH Analysis:

The pH was determined with a Fisher Accumet Model 610 A pH meter and a micro combination glass body electrode. The pH meter was recalibrated using two buffers of pH 4.00 and 7.00 before each analysis. Another precautionary measure involved determining the pH of the deionized-double distilled water that was added to each filter or impinger, to ensure that this would not lead to any errors. The actual pH measurement was accomplished by inserting the electrode into the 10 ml sample and recording the pH when a constant reading was obtained on the meter. Finally, the electrode was removed and washed with one ml of deionized-double distilled water.

Analysis for Nitrate Ion:

The nitrate analysis was done on the same sample that had been used for the pH analysis. The analysis was carried out with an Orion model 93-07 nitrate specific ion electrode, an Orion model 90-02 double junction reference electrode and a Fisher Accumet Model 610A pH meter working in the millivolt (MV) mode. The outer chamber of the reference electrode was filled with a 0.01M KCl solution and the inner and outer sections of the nitrate specific ion electrode were filled with the appropriate Orion solution (8). Finally, the slope of the linear portion of the concentration versus potential curve indicated that the electrode was responding to changes in the concentration of the nitrate ion correctly.

Before any measurements were taken, the pH meter was converted to the Millivolt (MV) mode by shorting out (joining) the reference and input terminals, changing the slope knob to 100%, the function knob from pH to MV and adjusting the reading to zero with the standardize knob. Once this had been accomplished, the nitrate specific ion electrode was attached to the input terminal and the reference electrode was connected to the reference terminal. The nitrate and reference electrodes were then inserted into the sample used in the pH analysis. Care was taken to ensure that the bottom of the nitrate specific ion

electrode was at an angle of at least 20° to the bottom of the beaker so that the bubbles which formed during the analysis could escape from under the electrode. This precaution was necessary because spurious readings were obtained when an air bubble was trapped under the electrode. The MV reading was recorded when the reading became constant. Finally, the electrodes were removed and rinsed with one ml of deionized-double distilled water.

The concentration of the nitrate ion in the sample was obtained from a calibration curve that had been prepared by plotting the MV reading obtained from sodium nitrate solutions containing different known concentrations of nitrate ion[1] against the nitrate ion concentration on semilog graph paper. The calibration curve is shown in Figure 1. The concentration of the nitrate ion in the mine air was calculated using the formula

$$C_{NO_3} \text{ in } mg/m^3 = \frac{C_{soln} \times 62.0 \times 10^3 \times \frac{11}{1000}}{V}$$

where C_{soln} is the concentration of the nitrate ion in moles per litre in the solution that was analyzed, 62.0×10^3 is the molecular weight of the nitrate ion in mg, 11/1000 is the volume of the sample in liters and V is the volume of mine air sampled in cubic meters.

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[1] These solutions were prepared by diluting a 1.00M sodium nitrate deionized-double distilled water solution with deionized double distilled water. The solutions used in making the calibration curve were 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} molar in nitrate ion.

Analysis for Sulfate Ion

The analysis for sulfate ion was accomplished using two completely different analytical procedures. One of the methods of analysis involved titrating the sulfate ions with Pb^{+2} ions and detecting the end point with a lead specific ion electrode. In this analysis, the outer chamber of the Orion Model 90-02 reference electrode was filled with a 1.0 molar sodium nitrate solution. No solutions were required for the lead specific ion electrode. The pH meter was converted to the MV mode and standardized using the method described in the section entitled Analysis of Nitrate Ion. In this case as well, the slope of the concentration versus potential curve indicated that the lead specific ion electrode was operating properly (13).

The analysis was accomplished by inserting the reference electrode and the lead specific ion electrode into the 36 ml methanol water solution that had been obtained by adding 24 ml of methanol to the 12 ml aqueous solution (the 10 ml used to extract the sulfate ions from the filter and the two, one ml volumes used to rinse the pH and nitrate electrodes). The methanol was used to ensure that the lead sulfate precipitated out of solution and the lead ion would not be detected by the lead specific ion electrode. A standard 2.50×10^{-3}M lead perchlorate solution was added 0.05 ml at a time from a 10 ml burette graduated every 0.05 ml. After each addition, the solution

was stirred for one minute with a magnetic stirrer and then the MV reading was taken from the pH meter. The titration was continued until a fairly large change followed by several fairly small changes in the MV readings had been observed. Finally, the MV readings were plotted against the volume of 2.50×10^{-3}M lead perchlorate solution that had been added and the end point for the titration was determined from the point of inflection in the titration curve (6). The amount of sulfate ion in the mine air, $C_{SO_4^=}$, was determined using the formula.

$$C_{SO_4^=} = \frac{V_{Pb} \times C_{Pb} \times 96.1 \times 10^3}{V_{Air}}$$

where V_{Pb} is the volume of lead perchlorate in liters used to titrate the sulfate ion, ie., the volume of lead perchlorate added at the end point minus the volume of lead perchlorate used to titrate a blank filter, C_{Pb} is the concentration of the lead perchlorate solution in moles/litre, 96.1×10^3 is the molecular weight of the sulfate ion mg and V_{Air} is the volume of mine air sampled in cubic meters.

The amount of sulfate ion in the underground samples was also determined by a spectrophotometric analysis. In some cases, this was done after the sample had been analyzed by the titrimetric method. This was done in this way to try to confirm the concentration of sulfate ion found

by the titrimetric procedure and in spite of some problems, the two methods were in reasonably good agreement. When the spectrophotometric analysis was done after the titrimetric analysis, a special procedure had to be used. In these samples, the methanol/water sample was transferred to a 100 ml round bottomed flask and the methanol and some of the water was removed under reduced pressure on a rotary evaporator. When the volume of the sample had been reduced to approximately 10 ml, the aqueous solution was heated to dissolve the lead sulfate that had formed in the titrimetric analysis. Then, the solution containing the lead sulfate was transferred into a 25 ml volumetric flask using a small glass funnel and a Whatman Qualitative 1 filter paper. This removed any particulate and the glass fibers from the original 25 mm filter. The round bottomed flask was rinsed several times with small amounts (approximately 5 ml) of hot deionized-double distilled water. These washings were also filtered through the same funnel and filter paper. This process was continued until 25 ml of filtrate had been collected in the volumetric flask. This 25 ml solution was then mixed with approximately 0.25 g. of Hellige Certified Reagent barium chloride crystals that had been specially prepared for determining sulfate ion. After the mixture had been stirred for one minute, the mixture was transferred to a 4 cm quartz U.V. cell and the absorbance resulting from the barium sulfate precipitate

was measured at 420 nm at 30 second intervals for five minutes. The maximum absorbance observed in the 5 minute period was taken as the absorbance of the solution. The absorbance of the barium sulfate solutions were measured on a Coleman-Perkin Elmer 124 double beam U.V. visible spectrophotometer. A 4 cm quartz U.V. cell containing a solution prepared by mixing 0.25 g barium chloride in 25 ml of deionized double distilled water was placed in the reference beam of the spectrophotometer, ie., was used as the reference cell for analysis. The instrument was always zeroed at 420 nm with deionized-double distilled water in both the reference and sample cells before each analysis to ensure that the instrument was working properly and the cells were clean.

The amount of sulfate ion in the 25 ml sample was determined from a calibration curve, Figure 6 that had been prepared by plotting the absorbance observed for solutions containing various known amounts of sulfate ion against the concentration of the sulfate ion in these solutions. Since the sulfate solutions that were used to prepare the calibration curve were obtained by diluting various amounts of a sodium sulfate solution containing 0.100 mg of sulfate ion per ml[1] to 25 ml, the concentration axis of the

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[1] This solution was prepared by dissolving 0.1479 of reagent grade anhydrous sodium sulfate in one liter of deionized-double distilled water.

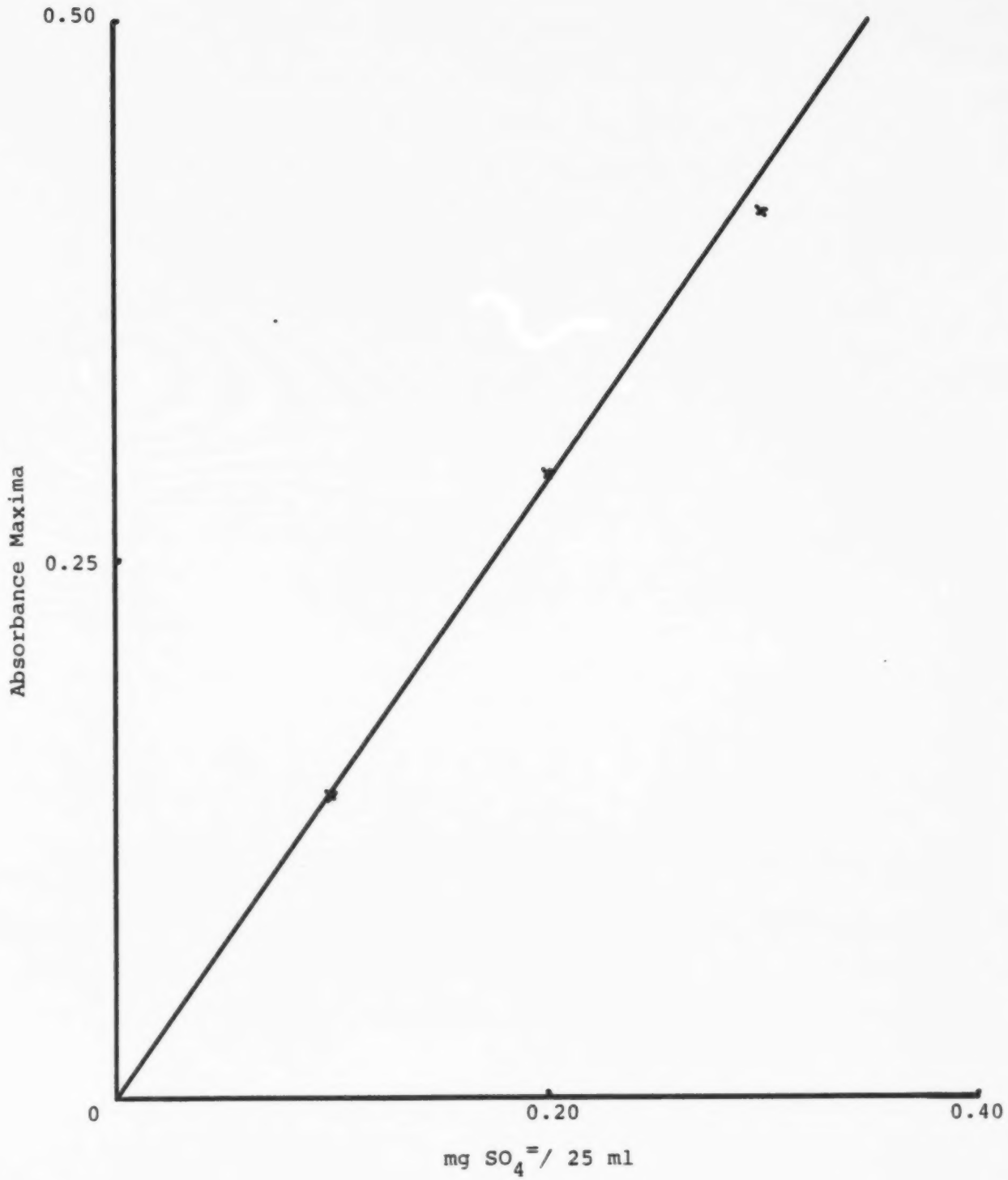

Figure 6. Calibration Curve for U.V. Spectrophotometer

calibration curve was in mg of sulfate ion/25 ml.

Once the amount of sulfate ion in mg/25 ml had been determined using the calibration curve, the concentration of sulfate ion in mg/m^3 in the mine air was calculated by dividing the sulfate ion concentration in mg/25 ml by the cubic meters (volume) of mine air sampled. When the analysis for sulfate ion was only done spectrophotometrically, ie., not after the titrimetric analysis of the sulfate ion had been completed, the procedure was different. In these cases the sample used in the pH and nitrate analysis was transferred into a 25 ml volumetric flask by filtering the solution through a small glass filter fitted with a Whatman Qualitative 1 filter paper. This removed the particulate and the glass fiber filter that had been used to collect the sample. Then the plastic beaker used in the pH and nitrate ion analysis was rinsed with a small amount of hot deionized-double distilled water and this solution was filtered into the 25 ml volumetric flask. This washing was continued until 25 ml of filtrate had been collected. Finally, the 25 ml solution was analyzed and the concentration of the sulfate ion in the mine air determined using the method described above.

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